I. X-RAY STUDIES OF THE BEHAVIOR OF RUBBER-BUNA S MIXTURES

II. X-RAY STUDIES OF ORIENTATION AND IMPREGNATION OF WOOD CELLULOSE

III. STUDIES OF GELATIN-SULFA DRUG SURGICAL MEMBRANES

BY

JOHN ARTHUR HOWSMON

A.B., Berea College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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PART I

X-RAY STUDIES OF RUBBER-BUNA S MIXTURES

INTRODUCTION

X-ray methods have been widely used in the study of both natural and synthetic rubber polymers. When unstretched, both natural and synthetic rubbers give an x-ray diagram consisting of a diffuse halo characteristic of an amorphous substance. When stretched, natural rubber crystallizes and gives a well defined x-ray pattern characteristic of the crystalline material while synthetic rubber of the Buna type shows no evidence of crystallization. Most of the x-ray data collected for natural rubber has been concerned with the evaluation of the intensity of the fiber diagram which appears when rubber is stretched. In general, the past work on natural rubber leads to the following conclusions: (1) the physical properties and performance of vulcanized rubber are related to the amount of crystalline material formed on stretching; (2) the amount of crystalline material formed on stretching depends upon the structural characteristics of the vulcanizates. The information which can be obtained from the x-ray patterns of the amorphous synthetic rubbers is limited, for the patterns show only a liquid structure and do not reveal the molecular basis of the rubber-like properties of the polymer.

This investigation was undertaken in order to determine the applicability of x-ray diffraction methods to the study of mixtures of rubber and Buna S; to obtain information regarding the behavior of such mixtures upon stretching; and if possible to correlate this information with the rubber content of the mixtures.

EXPERIMENTAL AND RESULTS

X-ray diffraction patterns were made using the technique described by Clark and LeTourneau[1]. Patterns prepared from samples which contained less than twenty-five parts of natural rubber in each one hundred parts of rubber indicated that no crystallization occurred at any elongation which could be obtained. In a mixture of equal parts of rubber and Buna S, the natural rubber component does begin to crystallize below

the elongation at which rupture occurs, but the fiber diagram obtained could not be quantitatively evaluated. No data which could be correlated with the physical properties or performance of these mixtures were obtained. Quantitative evaluation of the intensity of the fiber pattern of natural rubber should be possible for mixtures of high rubber content.

The position of the halo on the x-ray patterns of a series of samples of various natural rubber contents was found to be dependent upon the composition of the mixture. No definite relationship between halo position and rubber or Buna S content was found. Whether the observed halo was a single intensity maximum or the superposition of individual intensity maxima of rubber and Buna S could not be determined.

PART II

X-RAY STUDIES OF ORIENTATION AND IMPREGNATION OF WOOD CELLULOSE

INTRODUCTION

Present industrial research is faced with the problem of building to order a polymer having the properties required for some specific use. Among the natural products, cellulose most readily lends itself to such work for it can be modified by chemical treatment to give a wide range of physical properties. For structural uses wood is of primary importance. Shrinking and swelling with changes in moisture content is the most detrimental property of wood, and with the advent of molded products of wood, dimensional stability has become vitally important. In recent years the use of phenol-formaldehyde resins[2], heat[3], and pressure[4] have been predominant among the methods for overcoming this deficiency of wood.

This research was undertaken at the request of the Forest Products Laboratory in Madison, Wisconsin, in order to gain academic knowledge of the various treatments of wood. The specific problems involved are the following: (1) the study of swelling of wood by morpholine and pyridine to determine whether any compound formation occurs between the molecules of the swelling agent and the cellulose; (2) the study of distribution of the phenol-formaldehyde resin as a function of the resin concentration and the solvent used: and (3) the

study of the effects of heat and pressure on the orientation of the cellulose crystallites.

EXPERIMENTAL AND RESULTS

For the studies of swelling of cellulose x-ray patterns of ramie and wood which had been saturated with pyridine and morpholine were made with the long axis of the crystallites perpendicular to the x-ray beam. The agreement between the lattice dimensions of the untreated and swelled specimens indicated that no compound formation had taken place between the swelling agent and the cellulose. The swelling of cellulose by both pyridine and morpholine was classified as intermicellar.

Studies of wood impregnated with phenol-formaldehyde resin were carried out by a microradiographic technique. The best experimental results were obtained by the Co-K radiation and tangential sections of wood which were 0.015 inches thick. The microradiographs were found to be characteristic of the wood and the distribution of the impregnant. In general, alcohol soluble resins were found to be more evenly distributed on the surface of the wood cell walls than water soluble resins and are, therefore, more efficient in diminishing dimensional changes with variations in moisture content.

The orientation of the cellulose crystallites in normal wood and heated or compressed wood was compared by evaluation of the density distribution around the 002 diffraction ring on the x-ray patterns of the various specimens. Density measurements were made with a Leeds and Northrup recording microphotometer equipped with a rotating stage. In general, the degree of preferred orientation of fibers in compressed wood is less than that in normal wood. However, the changes in properties of compressed wood must be wholly attributed to the close packing and cementing of cellulose fibers caused by compression and not to differences in orientation between the normal and compressed woods. The degree of preferred orientation in heated wood is greater than that in normal wood. The small changes in orientation observed for the heated wood probably will not account for the increased dimensional stability of such specimens. A definite relationship between the degree of preferred orientation and the reduction in swelling was not possible because of the lack of sufficient data.

PART III

STUDIES OF GELATIN-SULFA DRUG SURGICAL MEMBRANES

In the present war the "sulfa" drugs have been invaluable in preventing infection of open wounds by providing a simple, immediate treatment. Many efforts have been made to extend this usefulness to surgery which in wartime is often done under primitive conditions. The major complicating factor is the toxicity of the drugs themselves. To obtain a surgical membrane with a minimum toxicity to human tissue, Griffith Laboratories attempted to couple the drug molecules to the gelatin used as the membrane base. Other components of the various membranes studied are urea, potassium iodide, glycine, and glutamic acid. Urea is a positive inhibitor of sulfanilamide; potassium iodide prevents the formation of scar tissue on open wounds; and glycyl and d-glutamine residues comprise thirty one per cent of the total amino acid content of the gelatin.

This x-ray investigation was undertaken to study these complex mixtures of sulfanilamide, sulfathiazole, sodium sulfathiazole and the gelatin with special attention to the possibility of bonding between the sulfonamide and the gelatin. No previous x-ray diffraction work on the crystal structure of the behavior of simple mixtures of these compounds has been reported.

EXPERIMENTAL AND RESULTS

X-ray diffraction patterns of the finely powdered samples were made by the powder technique described in books on x-ray analysis[5]. Ultraviolet absorption studies were carried out using the technique of Englis and Skoog[6].

The x-ray patterns of mixtures containing either sulfanilamide or sulfathiazole indicated that these drugs had been unaffected by any treatment to which they had been subjected. There was no evidence of any compound formation between the drug and the gelatin base.

X-ray patterns of mixtures containing sodium sulfathiazole sesquihydrate indicated one of the following: (1) that no

change had occurred; (2) that a new compound had been formed; or (3) that the original drug was no longer present in the crystalline form. The new compound was identified as anhydrous sodium sulfathiazole. The erratic occurrence of the original crystalline sesquihydrate was explained by the partial or complete solubility of the drug in the gelatin mixture. There was no evidence of any compound formation between the drug and the gelatin base.

Samples which contained sulfanilamide, sulfathiazole, and sodium sulfathiazole sesquihydrate were marked by the appearance of one extraneous interference in the x-ray pattern. The presence of this interference has not been explained. It cannot be caused by a compound formed between one of the drugs and the gelatin for it appeared in patterns of samples in which there was no gelatin present.

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VITA

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